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(21) International Application Number: PCT/EP94/01566 (22) International Filing Date: 13 May 1994 (13.05.94) (30) Priority Data: 9309946.3 14 May 1993 (14.05.93) GB (71) Applicant (for all designated States except US): EXXON CHEMICAL PATENTS INC. [US/US]; 1900 East Linden Avenue, Linden, NJ 07036 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): REYNIERS, Sylvian, Leontina, Edmond [BE/BE]; Peter Benoitlaan 2, B-1880 Kappelle-op-den-Bos (BE). FABRE, Jean, Claude [FR/FR]; 48, rue Champs-Lagarde, F-7800 Versailles (FR). (74) Agents: BAWDEN, Peter, Charles et al.; Exxon Chemical Limited, Exxon Chemical Technology Centre, P.O. Box 1, Abingdon, Oxfordshire OX13 6BB (GB).		(81) Designated States: JP, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: IMPROVED BASIC CALCIUM CARBOXYLATES (57) Abstract A solution in a plasticiser ester of a calcium superbase soaps in the form of calcium carbonate and calcium caboxylates, the carboxylic acids consisting of a mixture or otherwise of saturated organic carboxylic acids containing from 7 to 13 carbon atoms, having the following characteristics: a linear acid content of between 0 and 40 % by weight, a content of acids which are branched on carbon 2 of between 0 and 20 % by weight, and a content of acids which are mono- or polysubstituted on carbon 3 and/or on the carbons of higher rank, which is equal to or greater than 50 % by weight, is useful as a stabiliser for polyvinyl chloride, its manufacture by overbasing in the plasticiser medium is also covered.		

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Improved Basic Calcium Carboxylates

The present invention relates to new basic calcium carboxylate compositions, a method for their preparation and their use as polymer stabilisers, particularly stabilisers for polyvinyl chloride.

Traditionally lead salts have been used to stabilise polyvinyl chloride and it has been proposed to replace these with neutral calcium salts such as calcium oleate and calcium stearate. These salts however have relatively low calcium contents (of the order of 6%) so large amounts are needed to impart the stability.

Basic calcium carboxylates are known in many forms and are commonly used as additives in various lubricant systems and to impart anticorrosion properties to coatings such as temporary and permanent coatings for metals and as polymer stabilisers since they have a higher calcium level as possible in these products to reduce the amount of additive required to provide the desired calcium level. It has however proved difficult to develop a commercial process for the production of high calcium content calcium carboxylates prior to the use of various carboxylic acid mixtures as raw materials as described in our European Patent 0234 149.

The process of European Patent 0234 149 produces an oil solution of a high calcium content calcium carboxylate which is not useful in applications where the oil will act as a contaminant such as a plastics stabiliser. Furthermore the presence of the oil solvent increases the bulk and thus transportation costs. Other processes use organic solvents which can impart an undesirable odour to the final product.

There is therefore a need for a basic calcium carboxylate which may be incorporated into polymers, particularly as a stabiliser for polyvinyl chloride.

We have now developed new calcium superbase soaps formulations which do not possess the disadvantages of the known formulations, which have a high calcium content of the order of 10% or even higher, and which are compatible with polyvinyl chloride and the other components present therein.

The present invention therefore provides a solution in a plasticiser ester of a calcium superbase soaps in the form of calcium carbonate and calcium carboxylates, the carboxylic acids consisting of a mixture or otherwise of saturated organic carboxylic acids containing from 7 to 13 carbon atoms, having the following characteristics:

a linear acid content of between 0 and 40% by weight,

- a content of acids which are branched on carbon 2 of between 0 and 20% by weight, and
- a content of acids which are mono- or polysubstituted on carbon 3 and/or on the carbons of higher rank, which is equal to or greater than 50% by weight.

The invention further provides a process for the manufacture of such a solution comprising producing the overbased calcium superbase salt using the plasticiser ester as the reaction medium.

The calcium superbase soaps are preferably prepared from saturated C₈, C₉ and C₁₀ organic carboxylic acids which consist of isomeric mixtures and which are generally known as oxo acids. These oxo acids are characterized by a low linear acid content, generally less than or equal to 10% by weight, a low content of acids which are branched on carbon 2, generally less than or equal to 10% by weight, and a high content of acids which are mono- or polysubstituted on carbon 3 and/or carbons of higher rank, which is generally greater than 80% by weight. The oxo acids are obtained by hydroformylation of C₇, C₈ and C₉ olefins, followed by an oxidation.

Still more preferably, the calcium soaps according to the invention are prepared from the C₈ saturated carboxylic acid (that is containing 8 carbon atoms) marketed under the trademark Cekanoic, this acid consisting of an isomeric mixture of octanoic acids containing at most 10% by weight of n-octanoic acid, at most 10% by weight of C₈ acids which are branched on carbon 2 and at least 80% by weight of C₈ acids which are branched on carbon 3 and/or the carbons of higher rank. In fact, it has surprisingly been found that the use of this acid

makes it possible to obtain calcium soaps with a very high basicity of the order of 500 or higher.

Among the organic carboxylic acids which are also suitable for the present invention there may also be added the derivatives which are mono- or polysubstituted in the 3-position and/or of higher rank of the acids corresponding to heptanoic acid, octanoic acid, nonanoic acid, decanoic acid, undecanoic acid and dodecanoic acid. These include, for example, 3-methylhexanoic acid, isooctanoic acid, 4,5-dimethylhexanoic acid, isononanoic acid, 3,5,5-trimethylhexanoic acid, isodecanoic acid, 3-ethyloctanoic acid, isoundecanoic acid, 4-ethylnonanoic acid and isododecanoic acid. The mixture of one or more of the above-mentioned acids, whether mixed or not with their isomers, is also suitable for the present invention, it being understood that the content of linear acids does not exceed 40% and that the content of acids which are substituted on carbon 2 does not exceed 20%. We have found, in fact, that the linear acids and that the acids branched on carbon 2 lead to the formation of a viscous product, or to setting solid or, alternatively, to a precipitate which renders the product practically useless.

Suitable plasticiser ester are those typically used for plasticising polyvinyl chloride such as alkyl phthalates for example dioctyl phthalate, dinonyl phthalate and adipates and trimellitates. The ester should have a flash point above 120°C, and should be compatible with polyvinyl chloride and other additives such as phosphites, UV stabilisers, other metal containing additives particularly zinc stabilisers and other plasticisers traditionally used in PVC.

We have found that solutions of the superbase calcium carboxylate in the ester may be obtained containing as much as 10 wt% calcium, typically between 5 and 10 wt%, although the viscosity tends to be higher than desirable at the higher calcium levels.

The molar ratio of calcium to the organic carboxylic acid employed in the reaction is generally between 0.55 and 2, which corresponds to a basicity of between 1.1 and 4.

It should be recalled that the basicity is equal to the ratio of equivalents of calcium to the equivalents of carboxylic acids which are employed, that is to say, to the

molar ratio of the calcium concentration to that of the carboxylic acids, multiplied by 2.

5 In the calcium superbase soaps according to the invention, the promoters are used in a proportion of 1 to 25% by weight of final calcium salt, and preferably in a proportion of 5 to 15%.

The present invention will be better understood by reading the following example.

10 Example 1

Ca(OH)₂ is reacted with Cekanoic C₈ acid in the presence of injected CO₂ with methanol as promoter and Exxsol D40 as reaction diluent in the following proportions.

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- mass Ca(OH)₂ : 96.7 g
- mass Exxsol D40 : 258.7 g
- mass Methanol : 99.8 g
- mass Cekanoic C₈ : 144.0 g

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As described in European Patent 0234149, solid calcium salt is prepared by evaporating the solvent just by heating up the liquid sample in a cup exposed to air. Crystals are formed which then are crushed in a crucible. The resulted powder is dissolved in dinonyl phthalate and heated up to 80-120°C to give a
25 solution of 0.49 g solid in 20.07 g DINP. The solution was heated for 1 hour at 120°C and the solution remained clear and yellow with no smell of alcohol showing effective stabilisation.

Claims:

1. A solution in a plasticiser ester of a calcium superbase soaps in the form of calcium carbonate and calcium carboxylates, the carboxylic acids
5 consisting of a mixture or otherwise of saturated organic carboxylic acids containing from 7 to 13 carbon atoms, having the following characteristics:
 - a linear acid content of between 0 and 40% by weight,
 - 10 • a content of acids which are branched on carbon 2 of between 0 and 20% by weight, and
 - a content of acids which are mono- or polysubstituted on carbon 3 and/or on the carbons of higher rank, which is equal to or greater
15 than 50% by weight.
2. A process for the manufacture of such a solution comprising producing the overbased calcium superbase salt using the plasticiser ester as the
20 reaction medium.
3. A process for the preparation of the calcium superbase soaps according to claim 1 in which a calcium oxide and/or hydroxide is reacted, with stirring,
25 with carbon dioxide (or CO₂) which is bubbled through the reaction mixture and at least one organic carboxylic acid, in the presence of at least one promoter which makes CO₂ fixation easier and at least one catalyst, and in that the water formed during the reaction is removed, characterized in that the reaction is performed using a plasticiser ester as the reaction solvent,
30 and in that the said acid is a saturated organic carboxylic acid containing from 7 to 13 carbon atoms, in which the content of linear acids is less than or equal to 40% by weight, in which the content of acids branched on carbon 2 is less than or equal to 20% by weight, and in which the content of acids branched on carbon 3 and/or the carbons of higher rank is equal to or higher than 40% by weight.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER

IPC 5 C07C53/126 C08K5/09 C07C53/128 C07C51/41

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP,A,0 234 149 (SOCIÉTÉ CHIMIQUE DES CHARBONNAGES S.A.) 2 September 1987 cited in the application see page 3, line 34 - line 36 see claims 1-5	1
Y	WO,A,93 08246 (EXXON CHEMICAL PATENTS INC.) 29 April 1993 see page 4, line 17 - line 23 see claims 1-4	1
Y	US,A,3 639 264 (ROUSSOS ET AL.) 1 February 1972 see column 1, line 62 - line 68 see claims 1,4,8	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No.

PCT/EP 94/01566

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